INTRODUCTION

Copolymer structure has a marked effect on solution properties and thus behavioral characteristics of water-soluble copolymers utilized in enhanced oil recovery. Perhaps the most critical property of a candidate polymer for mobility control is its ability to maintain a large hydrodynamic volume (HDV) in the presence of mono- and divalent electrolytes. Additionally the structure and HDV of the polymer must be tailored to allow permeation through the reservoir rock without entrapment, adsorption, or shear degradation.

Hydrolyzed polyacrylamides or acrylamide/sodium acrylate copolymers have been used extensively in EOR; however, these polymers have been shown to be very susceptible to phase separation in the presence of divalent cations and undergo catastrophic viscosity losses at high electrolyte concentrations. Copolymers of acrylamide and sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS) display improved solution behavior in the presence of divalent ions. Extensive studies in our laboratories during the past few years have focused on tailored copolymer systems which maintain or increase viscosity in the presence of electrolytes including calcium ions1-21. In this paper, we report results for three polymer systems which appear to be especially promising for certain water-soluble applications including EOR. These are NaAMB/AM, an intramolecular calcium ion chelator; N-alkylAM/AM, an associative copolymer with hydrophobic domains; and low charge density ampholytic terpolymers. Certain copolymer compositions of each of the three possess unique solution characteristics and, thus potential commercial utility.

Copolymers of acrylamide with sodium-3-acrylamido-3-methylbutanoate, the AM/NaAMB series, are polyelectrolytes with high molecular weight. Unlike conventional acrylamide/sodium acrylate copolymers, however, viscosity loss in the presence of electrolytes is relatively low, apparently moderated by intramolecular stiffening effects. The AM/NaAMB copolymers like AM/NaAMPS show no phase separation in aqueous solutions of
calcium chloride even at 100°C. The high molecular weight, viscosity maintenance, and absence of phase separation at elevated temperatures in the presence of multivalent electrolytes render these polymers particularly attractive for mobility control in EOR.

In some instances the benefits of utilizing ultrahigh molecular weight (> 10 million) copolymers for viscosification are lost due to associated problems of entrapment (pore and channel clogging), shear degradation, and chromatographic effects. Field problems of dissolution, mixing, and injection without formation damage or plugging are often critical. As a result our group and industrial investigators have recently initiated research to develop low molecular weight copolymers which cooperatively associate in aqueous solutions to yield high viscosity. In theory, problems of channel and pore clogging and shear degradation would be averted since associations are reversible with increasing shear stress. "Hydrophobic" associations of this type, although widely recognized in biopolymers and associative thickeners for coatings are poorly understood.

The acrylamide/N-alkyl acrylamide copolymers in this report contain low mole percentages of C₈, C₁₀, or C₁₂ substituted monomers. The copolymerizations were conducted in an aqueous medium containing high concentrations of surfactant. This method has been called "micellar" polymerization. Ongoing research in our laboratories leads us to believe that micellar copolymerization may result in somewhat blocky structures. Above a critical polymer concentration the hydrophobic domains of separate polymer chains may associate. This concentration appears to be significantly lower than the critical concentration required for chain entanglement in non-associating polymers. Increasing ionic strength and increasing temperature appear to enhance domain formation while increasing shear disrupts domain association. Although the above properties are certainly intriguing, the mechanism of association must be clearly elucidated in order to tailor macromolecules of this type for EOR and related applications.

Ampholytic polymers offer some unique characteristics which might be utilized in viscosity modification and/or permeability alteration during EOR processes. By careful molecular tailoring, charged moieties which can be responsible for large hydrodynamic volume changes with the addition of external electrolytes may be placed strategically along the macromolecular backbone. To date, few studies have been directed toward energy-related polyampholyte applications. In this paper we report initial studies on promising low charge density polyampholytes.

One additional polymer system which will not be detailed in this report is a surfactant-like polymer which in aqueous solution has little viscosity and forms independent micelles. Upon addition of hydrocarbons to the aqueous polymer solutions, a viscosifying effect is observed. Such a system might be potentially designed to act both as a surfactant and a viscosifier for mobility control in EOR.